A **LJEST**

Catalytic performances of mesoporous chromium silicates in liquid phase oxidation of toluene

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ABSTRACT/RESUME

Abstract: The liquid phase oxidation of toluene using peroxide hydrogen (H_2O_2) as oxidant was investigated over mesoporous chromium silicates MCrS(n) (n=Si /Cr) with different Si/Cr molar ratio (Si/Cr =20 and 60). MCrS (n) were prepared in strong acidic media by assembly of preformed CrS1 precursors with triblock copolymer of the pluronic type (P123) by a two steps procedures.
They were characterized by X-ray powder diffraction (XRD), N_2 adsorption, Fourier-transform infrared spectroscopy (FT-IR), diffuse reflectance ultraviolet-visible spectroscopy (DRUV–vis) and electron paramagnetic resonance spectroscopy (EPR). The catalytic performances were compared with those of CrSBA-15 20 (Si/Cr =20). The MCrS catalysts exhibited higher catalytic activity than CrSBA-15 20, the toluene conversion increased with an increase in chromium content. The oxidation occurred mainly at the aromatic ring, as the cresols isomers were the dominant products. Increasing the chromium content caused a decrease in the selectivity to cresols. The highest activity was observed over MCrS (20). Moreover, this catalyst was very stable after three cycles of reuse.

I. Introduction

The selective catalytic oxidation of organic compounds using environmentally friendly and cheap oxidants, such a molecular oxygen and aqueous H_2O_2, and heterogeneous, easily recyclable catalysts is challenging goal of fine chemistry [1-6]. The titanium silicalite (TS-1) was the first example of a redox molecular sieve, which exhibited an activity in the liquid phase oxidation of hydrocarbons with hydrogen peroxide under mild conditions [7-10].
The success of TS-1 motivated various research groups to investigate a wide range of metal-incorporated microporous and mesoporous molecular sieves as oxidation catalysts, e.g., chromium substituted silicalite-1 (CrS-1), aluminophosphates (CrAPOs), Cr(VI)-grafted mesoporous polyaniline (Cr-MPANI) and VOHPO4 dispersed on mesoporous silica KIT-6

for the oxidation of alkylaromatics, alcohols and allylic oxidation of olefins [11-16]. The VOHPO4 dispersed on mesoporous silica KIT-6 exhibited 17.76% toluene conversion and 69.24% benzaldehyde selectivity [16].
A growing interest can be observed for the design and synthesis of metal-containing mesoporous materials in the last two decades, in order to overcome the diffusion limitations in zeolite micropores [17–19].However, although that the heteroatoms are incorporated into mesoporous materials, they do not exhibit as high catalytic activity as in the zeolites, which can be ascribed to the amorphous nature of the pore walls.
Various synthetic routes have been investigated in the last years in order to introduce some structural order into the amorphous pore walls of mesoporous catalysts and to enhance their activity for different reactions [20-23].
In the current study, mesoporous chromium silicates (MCrS) were investigated for the liquid

phase oxidation of toluene using H2O2 as oxidant. In addition, the MCrS(n) (n) (n=Si /Cr) with different Si/Cr molar ratio (Si/Cr =20, 60) were prepared in strong acidic media by assembly of preformed CrS1 precursors with triblock copolymer of the pluronic type (P123) by a two steps procedure. To the best of the authors knowledge' this is the first report investigating mesoporous chromium silicates, synthesized via this procedure, as catalyst for selective liquid phase oxidation.

II. Materials and methods

II. 1. Mesoporous materials preparation

Mesoporous chromium silicate (MCrS) were synthesized according to the following procedure developed by Xiao for the synthesis of mesoporous ferrisilicate [21]:
(1) the zeolite precursor solution with CrS-1 building units was prepared by dissolving a calculated amount of chromium nitrate, in order to obtain a well defined Si/Cr ratio equal to 20 and 60, in 12 mL H2O.Then, 6 mL of tetapropylammonium hydroxide aqueous solution was added dropwise, followed by the addition of 5.6 g of tetraethyl-orthosilicate under stirring. The mixture was transferred into an autoclave at 100°C for 3 h to get precursor solution.
(2) In order to obtain the mesophase, 2.5 g of EO20PO70EO20 (Pluronic 123) was dissolved in the solution of 60 mL of H2O and 15 mL of 10M HCl, followed by addition of the precurseur solution obtained in step one. The mixture was stirred at 40 °C for 20 h, and then transferred into autoclave for additional reaction at 100 °C for 24 h. After cooling to room temperature the solid product was filtered and dried at room temperature in air (23°C ± 2°C). Template removal was achieved by calcination in air at 550 °C for 5 h (heating rate: 1 °C/min). The samples were called MCrS (20) and MCrS (60).
For comparison purposes, a reference chromium-substituted mesoporous SBA-15 (molar ratio Si/Cr in synthesis gel = 20) was prepared by conventional hydrothermal synthesis as follows:
9 mL of tetraethyl-orthosilicate and the calculated amount of chromium nitrate, in order to obtain a well-defined Si/Cr ratio equal to 20, were added to 10 mL of HCl aqueous solution at pH 1.5. This solution was stirred for over 3 h and then added to a second solution containing 4 g of amphiphilic triblock copolymer poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) (EO20PO70EO20 (pluronic 123 from Aldrich) in 150 mL of HCl aqueous solution at pH 1.5 at 40 °C. The mixture was stirred for another 1 h and finally crystallized in a Teflon-lined autoclave at 100 °C for 2 days. The solid product was filtered

and dried at 100 °C. Template removal was achieved by calcination in air at 500 °C for 4 h (heating rate: 1 °C min^{-1}). The sample was called CrSBA-15 20.

II. 2. Characterization

The XRD diffractograms were performed on a D5000 Siemens powder diffractometer equipped with copper anode. The scattering intensities were measured over an angle range of 0.5°<2θ< 3° with a step size Δ (2θ) = 0.02° and a step time of 8 s.
The N2 adsorption/desorption isotherms were measured on a Micromeritics ASAP2010 at liquid N2 temperature. Specific surface areas of the samples were calculated from the adsorption isotherms by the BET method and pore size distribution from the desorption isotherms by the BJH method.
Infrared spectra were acquired from KBr pellets in the 1200-400cm-1 range using a Perkin Elmer FT-IR spectrophotometer.
The DRUV–vis spectra were recorded using a Cary 5000 spectrometer in the wavelength range from 200nm to 800 nm.

II. 3. Catalytic reactions

The oxidation reactions were carried out batchwise in a glass reactor as reported by Singh [14]. Typically, 0.25 g of catalyst, 2.5 g of toluene, 3.45 g of H2O2 and 10 mL of acetonitrile were introduced. The reaction was continued for 24 h at 80°C.

III. Results and discussion

III.1. Characterization of mesoporous materials
The characterization of MCrS (n) materials was fully investigated in our previous paper [24]
X ray diffraction patterns of the SBA-15 and MCrS (60) materials (not shown) indicate that these materials are hexagonally ordered mesostructure. MCrS (60) is not as highly ordered as SBA-15. The absence of diffraction peaks at 2θ > 10 suggests that the MCrS material is pure mesoporous phase without bulky zeolite crystals or chromium oxides.
The IR spectra of MCrS (Fig. 1) show a peak at near 550 cm-1, which is characteristic of 5-rings of zeolite structure.
In accordance with the nomenclature defined by IUPAC [25] typical irreversible type IV adsorption isotherms (not shown)were observed for SBA-15 and MCrS materials, which indicate mesoporous structure of these materials. The pore size distribution (not shown) of the MCrS materials is broader than that of the SBA-1 5 material, which could be ascribed to some disorder in the product.
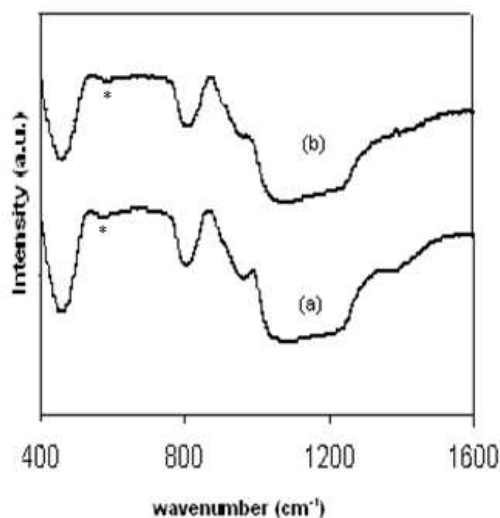
Figure 1. *FT-IR spectra of as-synthesized MCrS (60) (a), (MCrS (20) (b)*

Structural and textural parameters are reported in table 1. It is important to note that that the pore walls of MCrS materials are much thicker than those of SBA-15 prepared from the same conditions, which is ascribed to that the nanoclustered CrS-1units used for MCrS have stronger rigidity and larger volume than nonstructured silicon species used in conventional synthesis of SBA-15. Therefore the assembly of nanoclustered CrS-1 units needs more space to join with one another.

The yellow color of all calcined MCrS samples is due to higher valence chromium ions, viz., chromate and/or polychromate ions, in the tetrahedral environment [26].

The DR UV-vis spectra of calcined MCrS (20) and MCrS (60) samples (Fig. 2) indicate the presence of characteristic bands of O-Cr (VI) charge transfers of the chromates species [28], and Cr(VI) polychromate [27, 28]. These results indicate that high chromates exist in calcined CrSM materials. Cr (III) species are also observed in CrMCM-48 with high Chromium content [28].
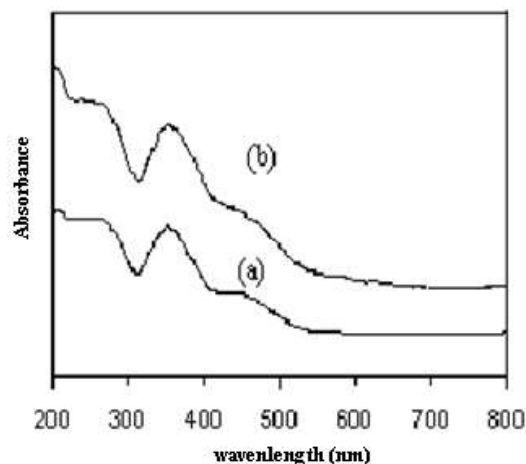

Figure 2. *The diffuse reflectance UV-visible spectra of calcined MCrS(60) (a), MCrS (20) (b)*

III. 2. Catalytic activity for toluene oxidation

The activities of MCrS and CrSBA-15 20 catalysts in liquid-phase oxidation of toluene, using hydrogen peroxide as oxidizing agent are reported in table 2. MCrS catalysts exhibit higher catalytic activity than CrSBA-15 20. In contrast, CrS-1 catalyst (Si/Cr = 52) is completely inactive under the same reaction conditions and shows low activity using TBHP as oxidant [14] (table2). Other zeolites such as TS-1 and CrS-2 have failed to oxidize alkylarenes [29]. Results can be explained by the stabilisation of the chromium ions in the mesoporous matrix [30].

It can also be seen from this table that for the mesoporous MCrS and CrSBA-15 20 catalysts the oxidation occurs mainly at the aromatic ring, as the cresols isomers are the dominant products. Increasing the chromium content caused a decrease in the selectivity to cresols. By contrast to CrS1 catalyst, no benzoic acid and dibenzyl formation is observed over MCrS and CrSBA-15 20 (table 2). In the case of the mesoporous MCrS and CrSBA-15 20 catalysts, the mesopores allow the increase of the products diffusion which prevents the formation of benzoic acid and dibenzyl through secondary reaction; Benzoic acid is formed by the subsequent oxidation of benzaldehyde (which is formed from benzyl alcohol). The high selectivity to cresols over MCrS and CrSBA-15 20 catalysts can also be explained by the mesopores which facilitate the diffusion of these bulky molecules.

Table 2 shows that toluene conversion increases with an increase in chromium content, this result is in agreement with those published by Selvam [26] in the liquid-phase oxidation of cyclohexane over mesoporous (Cr)MCM-41 molecular sieves using H2O2 as oxidant. It can be seen from table 2 that the activity of the most active catalyst MCrS (20) remained almost unchanged after three cycles of

reuse, which indicate a high stability of this catalyst.

Table 1. Textural properties of purely siliceous SBA-15 and MCrS

Sample	Si/Cr Gel mixture	BET area $(m^2\,g^{-1})$	Pore volume $(cm^3\,g^{-1})$	Pore diameter (nm)	d_{100} (nm)	Unit cell Parameter a (nm) [a]	Pore wall thickness t (nm) [b]
SBA-15 Calc.	—	883	1.01	5.90	9.59	11.09	5.17
CrSM calc	20	640	1.64	4.9	/	/	/
CrSM calc	60	808	1.38	4.6	10.53	12	7.4

(a): Unit cell Parameter a = $2\,d_{100}/\sqrt{3}$
(b): Pore wall thickness, t = a- pore diameter

Table 2. Catalytic oxidation of toluene by mesoporous chromium silicate

Catalysts	BET area (m^2g^{-1})	Conversion (%)	Products selectivity					
			Benzaldehyde	benzyl alcohol	Benzoic acid	Dibenzyl	o-cresol	p-cresol
MCrS (60)	808	25.1	22	11	/	/	36	31
MCrS (20)	645	63.2 (1st Run)	40	6	/	/	28	26
		58.4 (2nd Run)	13	5	/	/	20	62
		62,0 (3rd Run)	20	10	/	/	33	37
Cr-SBA-15 20	628	46.8	29	/	/	/	59	12
CrS-1 [c]	336	18.4	23	5	25.7	45.1	0.4	0.5

c: using TBHP as oxidant [14]

The maximum adsorption capacity of apricot stonesto bind chrome(VI) ions was compared with other biosorbents. From Table 2, one can see that adsorption capacity value of apricot stones is lower than that of banana peel [8], bagasse fly ash [9] and rice husk [13]. On the other hand, this value is higher or considerably greater than other reported biosorbents [10].

IV. Conclusion

Characterization results of mesostructured chromium silicates MCrS synthesized in strong acidic media by assembly of preformed CrS1 precursors with triblock copolymer, indicate that the calcined MCrS materials contain Cr(V) and Cr(VI) under low and high Cr content and that the mesoporous walls contain the MFI structure building units. In the Liquid-phase oxidation of toluene, mesoporous MCrS materials show greater activity in comparison with mesoporous CrSBA-15 and microporous CrS-1 which is completely inactive under the same reaction conditions and shows low activity using TBHP as oxidant [14]. The highest activity was observed over MCrS (20).

Moreover, this catalyst was very stable after three cycles of reuse. Therefore, it is of much interest as a potential catalyst for the oxidation of alkylarenes with hydrogen peroxide under mild conditions.

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